as the plate thickness increases. Resolutions of 30—40 line pair/mm have been measured for other 0.250-mm-thick plates. The time required to store an image for present FE-PC prototypes is limited by the properties of the PVK photoconductive film. The insertion loss of the FE-PC device, with the ceramic poled to saturation remanence prior to image storage, was about 7 dB.

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Precipitation of Si from the Al Metallization of Integrated Circuits

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The Al metallization of integrated circuits is known to dissolve $\frac{1}{2}\%$ or more Si, but the ultimate location of this Si has been uncertain. An electron microprobe operated at low beam energy so as to penetrate only the upper portion of the metallization was used to follow the movement of dissolved Si on cooling after the "forming" heat treatment. Dissolved Si substantially less than a diffusion length from the substrate was found to regrow there; elsewhere the Si forms precipitates in the Al matrix, preferentially near the free surface of the Al.

Much of the Al metallization of integrated circuits becomes saturated with Si during the "forming" heat treatment. On cooling from the forming temperature, the dissolved Si becomes supersaturated and should precipitate. The present study was undertaken to determine where the precipitation occurs and the dominant kinetics.

The prototype integrated circuit employed is indicated in cross section at the top of Fig. 1 and has been described previously.[1] The thermally grown oxide was about 0.3 μ thick, the Al evaporation about 3 μ thick, and cuts in the oxide about 75 μ wide were produced photolithographically in the pattern of a cross. This cross pattern appears in Fig. 1, in the view labelled "after slow cool", though this is not an ordinary optical photomicrograph, as will be explained.

Specimens were heated in dry argon at $530 \pm 5\,^{\circ}C$ for 1 h or more to saturate the Al metallization with Si in the vicinity of each cross. At the end of the saturation treatment, specimens were cooled according to a variety of cooling schedules. "Slow cool" means that the tube furnace containing the specimen was cooled at about $10\,^{\circ}C$/min to $275\,^{\circ}C$, whereupon the specimen was rapidly removed from the furnace, in perhaps 2 sec, and dropped onto a cool asbestos surface. At the other extreme, the "quench" specimens were rapidly removed directly from the $530\,^{\circ}C$ furnace. Also employed was a "step cool" schedule, in which specimens were saturated at $510\,^{\circ}C$, then rapidly placed in a cavity in a copper block held at $435\,^{\circ}C$ and held there for a specified time τ, then rapidly cooled to room temperature.

Specimens were examined in an electron microprobe, set to detect SiK_α radiation and using typically a 10-keV 10^{-7}-A electron beam. Such a low-energy beam excites SiK_α fluorescence only in the upper portion of the metallization as suggested in the sketch of Fig. 1. Prior to heat treatment, no Si could be detected in the metallization. After heat treatment, Si concentrations [Si] averaging ~ 1% were found to be present, though the Si distribution was quite uneven. By finely focusing the electron beam, nominally to a diameter of 0.2 μ, small-scale structure in [Si] was exhibited.

The most striking result obtained in the study was the obvious relation between a pattern cut in the oxide and the location of Si precipitates. The photograph of the slow cool specimen in Fig. 1 shows this most clearly. The same cross pattern can also be discerned in the original photograph of the quench specimen, but is more evident in Fig. 2, which indicates that the average [Si] in the metallization directly overlying the substrate Si is less than for that overlying the SiO_2.

A similar result was observed in step cool specimens. When the holding time τ at the intermediate temperature was 15 sec, a precipitation pattern similar to that of the "quench" specimen was obtained, though slightly coarser. When $\tau = 60$ sec, however, precipitates over the SiO_2 were significantly coarser and most precipitates over the substrate (i.e., in the cross pattern) disappeared.

Some idea of the depth distribution of precipitates was obtained by repeatedly photographing, with SiK_α fluorescence, the same area of the slow cool specimen shown

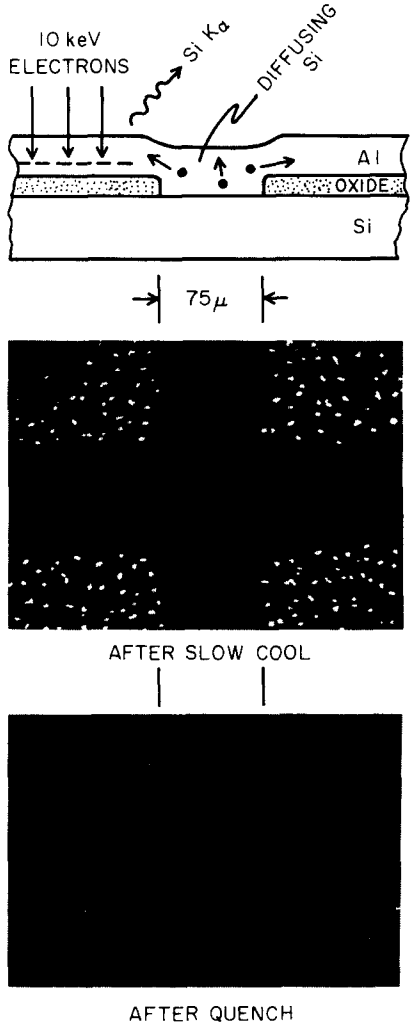

FIG. 1. Cross section of a specimen, schematized to illustrate the experiment, together with top views of two specimens ("after slow cool" and "after quench") as exhibited by an electron microprobe tuned to the SiK_α fluorescence. Si precipitates, formed in the Al metallization during heat treatment, appear as white particles in the microprobe photographs. (The horizontal distortion of precipitate shape in the last photograph is an artifact arising from the resolution time of the scanning electronics.)

in Fig. 1, but at varying beam voltages. These photographs indicate that there is a predominance of precipitates near the top, or free, surface of the Al.

These results can be interpreted in a simple way by comparing the diffusion length for Si in Al, $(Dt)^{0.5}$, where D is the diffusivity and t is time, to the distances the dissolved Si must travel to reach a growth surface. Under quench conditions, for example, the estimated effective diffusion length of $(\int D\,dt)^{0.5} \simeq 1-2\ \mu$ is somewhat less than the 3-μ thickness of the metallization. Thus only some of the dissolved Si in the cross region is able to diffuse to the substrate, and hence out of view

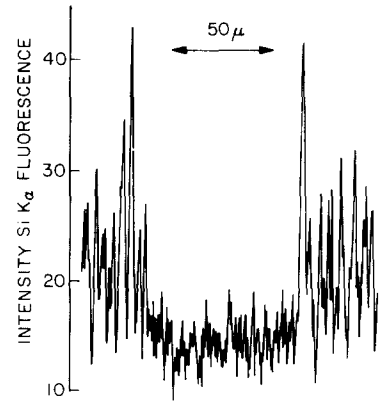

FIG. 2. Profile of Si concentration across the quenched specimen of Fig. 1. The 50-μ marker is centered over an oxide cut. Microprobe traversed at approximately 55 μ/min.

for the microprobe operated at 10 keV; the remainder of the dissolved Si is unable to go the distance to the substrate and remains as the very fine precipitates profiled in Fig. 2. On the other hand, for the slow cool specimen the estimated effective diffusion length is ~30 μ, and dissolved Si in the 3-μ-thick metallization has ample opportunity to diffuse to the substrate. Thus no Si remains in view of the microprobe in the cross region of the slow cool specimen.[2]

Over the SiO_2 layer, however, no pre-existing nucleus for Si growth is present. During cooling the dissolved Si becomes increasingly supersaturated until a critical supersaturation for nucleation of Si crystals is reached. On further cooling, the most energetically favored nuclei continue to grow, while other nuclei, roughly within a diffusion length of the favored ones, disappear. This is the coarsening phenomenon evident in Fig. 1.

Probably the most important consequence of the present experiments is to show that solid-state growth of a semiconductor can readily occur at the metal-semiconductor interface under commonly used conditions of heat treatment. This growth on the substrate could be expected to affect electrical characteristics significantly, provided the growth is thick enough. Indeed, with sufficient thickness, one imagines the growth should be comparable to those obtained by vapor-phase or liquid-phase epitaxy in forming p-n junctions or good Ohmic contact.

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[2] Actually, a small [Si], roughly corresponding to the solubility at 275°C, can be detected by statistical counting at a fixed location.